NO_x Control & Measurement Technology for Heavy-Duty Diesel Engines

W.P. Partridge, J.A. Pihl
Oak Ridge National Laboratory

S. Joshi, N. Currier, R. Daya, K. Kamasamudram, A. Yezerets
Cummins Inc.

H. Hess, H.-Y. Chen
Johnson Matthey Inc.

DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 13, 2019; Arlington, VA

VTO Program Managers:
Gurpreet Singh & Ken Howden

ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

ace032_Partridge_2019_o

Overview

Timeline

- ***New Project***
  - 2018 VTO AOP Lab Call
  - AOI-1E: Low Temperature Emissions Control (Heavy Duty)
- Year 1 of 3-year
  - Start Date: Oct. 1, 2018
  - End Date: Sept. 30, 2021
  - Percent Complete: 16%

Barriers

- From **21st CTP Research Blueprint**:
  - Emission control cost
  - Low-temperature emission control
  - Robustness in real-world application
- From **U.S. DRIVE Roadmap**:
  - Low-temperature emission control
  - Compliance via Real Driving Emissions (RDE)
  - Emissions control durability

Budget

- 1:1 DOE:Cummins cost share
- FY19 DOE Funding: $450k
  - DOE share: $450k
  - Cummins share: $450k (in kind)

Partners

- ORNL & Cummins Inc.
- Johnson Matthey (participant)

Milestones

FY	Qtr	Milestone & Objectives	Status
2018	4	Experimentally characterize reaction steps for a commercial SCR catalyst, over a conditions relevant to model development	complete
2019	2	Outline structure for half-cycle-based model	complete
2019	3	Protocol experiments on degreened commercial catalyst	on track

Responses to 2018 Review Comments *(Previous Project)*

- Desire to have more project participants
  - *Catalyst supplier formally incorporated as a participant*
  - *Beyond their traditional contributions via the separate CMI-JMI partnership*

- Integrate kinetic model with a thermal model
  - *Cummins' In-House Detailed Model contains kinetics and heat transfer*

Collaborations and Coordination

- **ORNL:** Bill Partridge
- **Cummins:** Saurabh Joshi
- **Johnson Matthey:** Howard Hess
  – Formally included in CRADA and Project documentation

Teamwork & Roles

ORNL	Cummins	Johnson Matthey
• Diagnostics • Measurements	• Modeling • Field ageing	• Model catalyst samples

Joint
- Planning
- Results interpretation
- Monthly+ telecons

- **Interactions with technical community**
  – 1 archival publication
    W.P. Partridge, S.Y Joshi, J.A. Pihl, N.W. Currier (2018). "New Operando Method for Quantifying the Relative Half-Cycle Rates of the NO SCR Redox Cycle Over Cu-Exchanged Zeolites," Applied Catalysis B: Environmental, **236**, 195-204. doi.org/10.1016/j.apcatb.2018.04.071
  – 1 invited book chapter
  – 3 presentations (1 invited)

Key Challenge Addressed by Project

- Efficient catalyst performance under ***Field-Aged*** & ***Low-Temperature*** conditions
  - How does field ageing impact SCR reaction network
  - Mechanistic impact of 'low-temperature' SCR formulations
  - Improve catalyst durability under ***Real-World Driving Conditions***

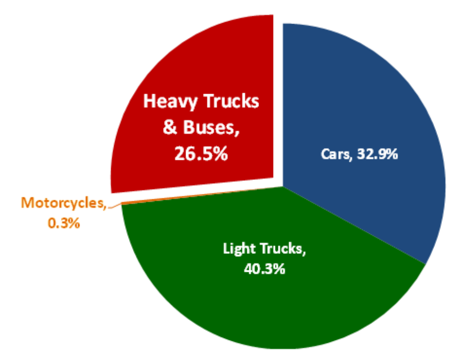
Relevance

- Durability advances critical to meeting increasing manufacturer warranty requirements
  - Useful Life: compliance on certification drive cycle
  - Warranty: compliance under real-world-driving conditions
    - E.g., Lower temperatures, higher space velocities, & other real-driving 'off-cycle' conditions

- Better catalyst performance allows engine to be optimized for fuel efficiency

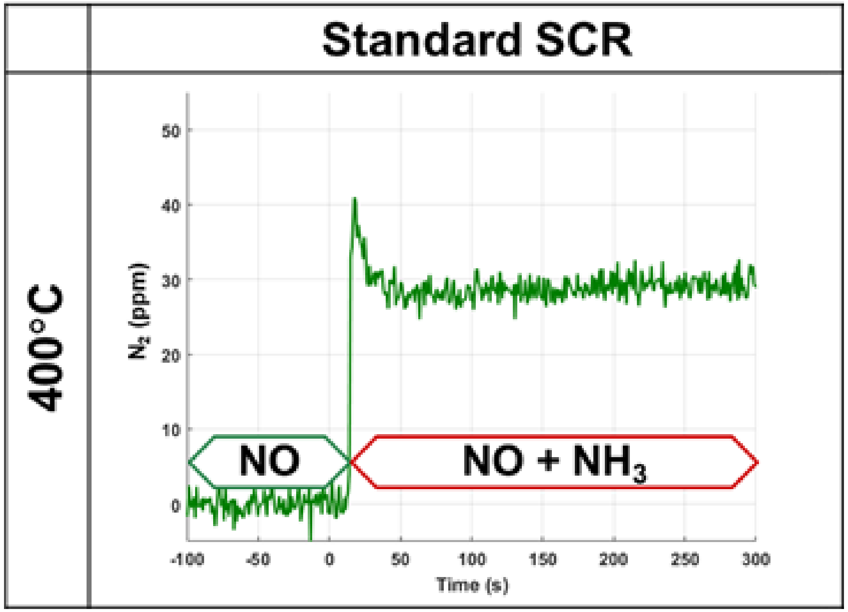
Heavy Heavy Duty Emissions Regulations				
Current		2022	Projected '26/'27	
CARB/EPA	CARB			
Useful Life (miles)	***Warranty*** (miles)	***Warranty*** (miles)	Useful Life (miles)	***Warranty*** (miles)
435,000 (10yr, 22k hr)	***100,000*** (5yr, 3k hr)	***350,000*** (5yr)	1,200,000	***800,000***

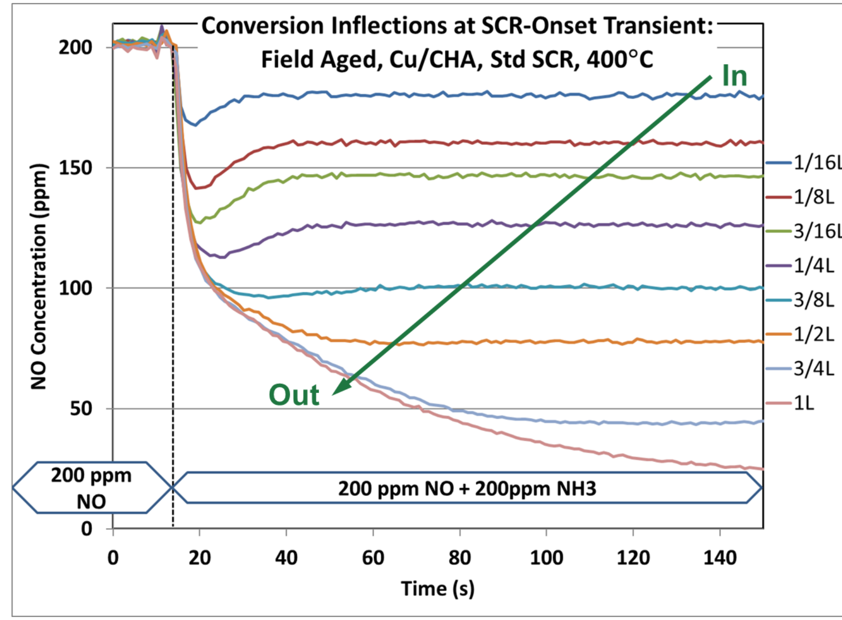
Rapidly Increasing Warranty & Useful-Life Demands



On-Highway Petroleum Use
(Source: Transportation Energy Data Book)

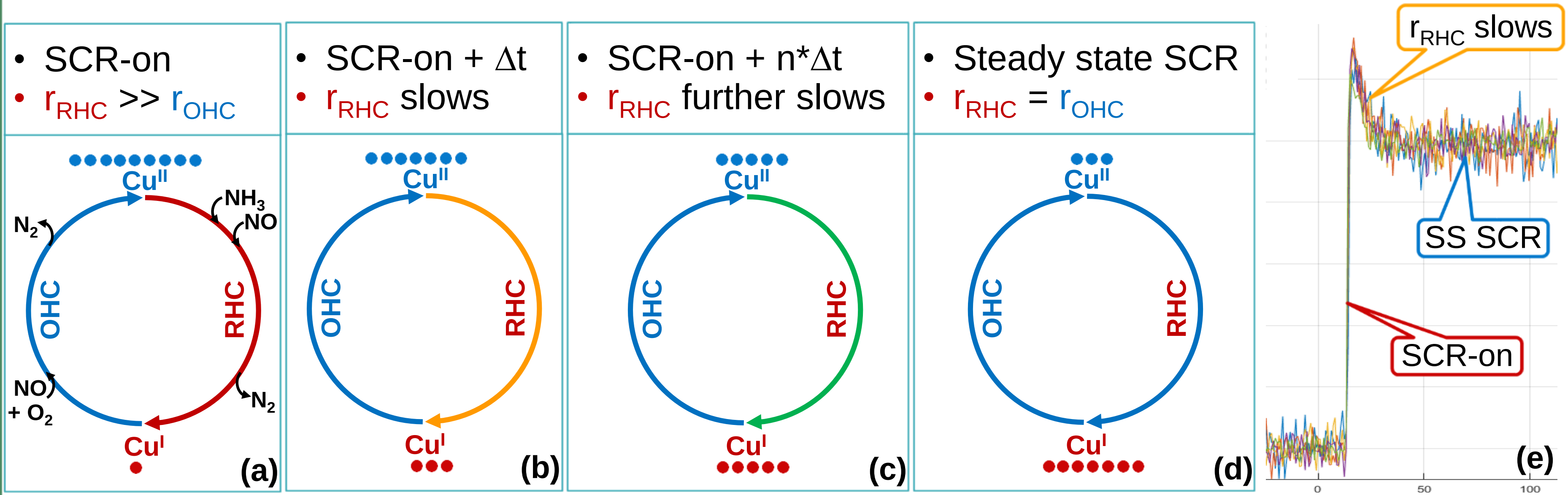
Using Transients to Improve Catalyst Performance





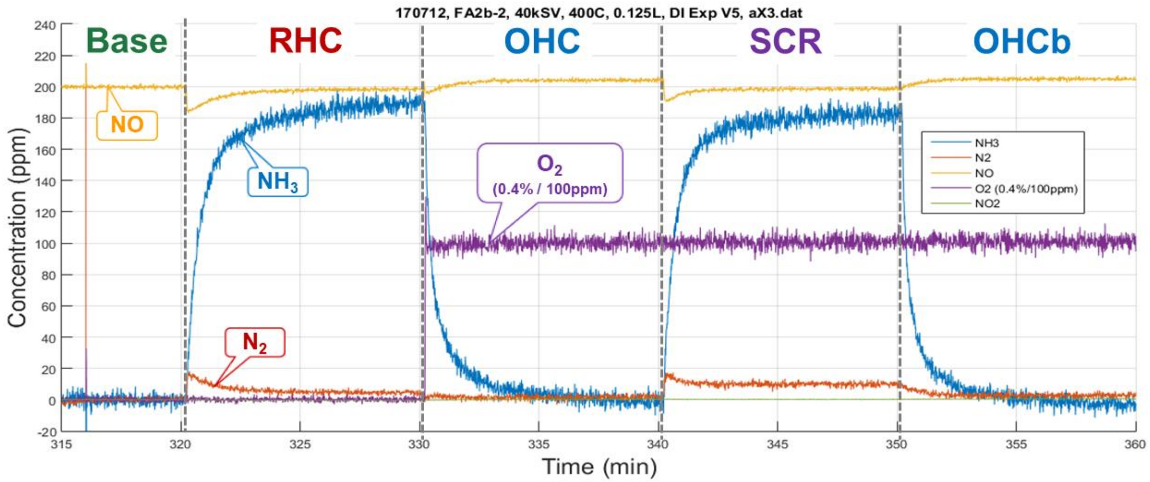
- Conversion Inflections (CI) can occur with Cu/SCR catalysts at SCR onset
  - Fast conversion onset & Slower conversion degradation to steady state level
- CI nature varies catalyst conditions
  - SCR type and temperature
  - Catalyst location (local concentrations and space velocity)
  - Catalyst age
- ***Transient CI can be used to understand kinetic origins of catalyst performance***

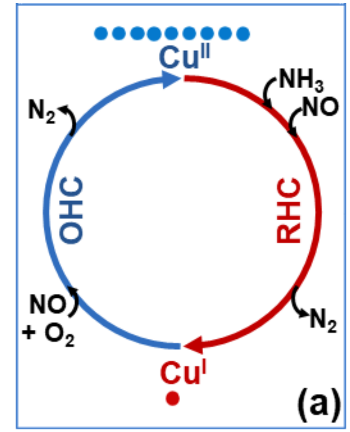
CI Transient Shape Reflects SCR Kinetic Parameters



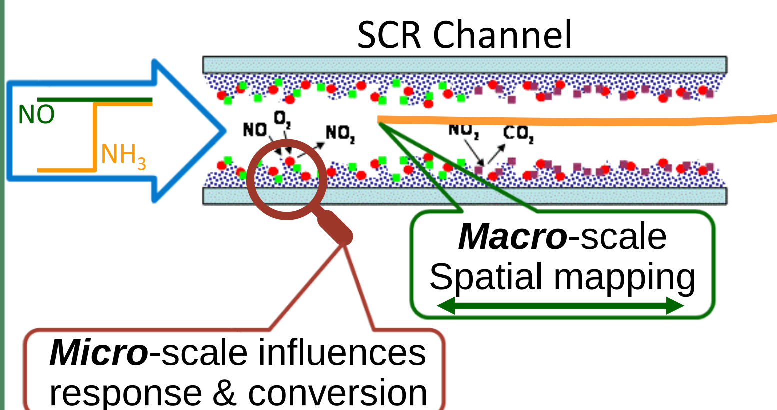
- Cu SCR can be viewed as cyclic Cu reduction and oxidation
  - **RHC: Reduction Half Cycle** – oxidized Cu (Cu^{II}) is reduced to Cu^{I}
  - **OHC: Oxidation Half Cycle** – Cu^{I} is reoxidized to Cu^{II} completing the cycle
- Half-cycle rate imbalances induce CI at SCR onset
  - CI occurs when the RHC rate is faster than the OHC rate; $r_{RHC} > r_{OHC}$
  - r_{RHC} progressively slows to match r_{OHC} at steady state
- ***Detailed CI Shape depends on half-cycle kinetic parameters***
  - ***Use to study kinetic impact of catalyst ageing & formulation***

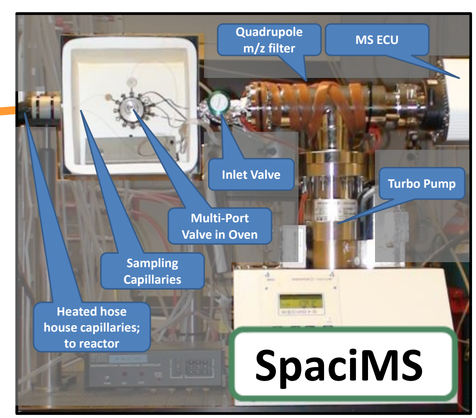
CI Transient Response can be Measured for Each Half Cycle

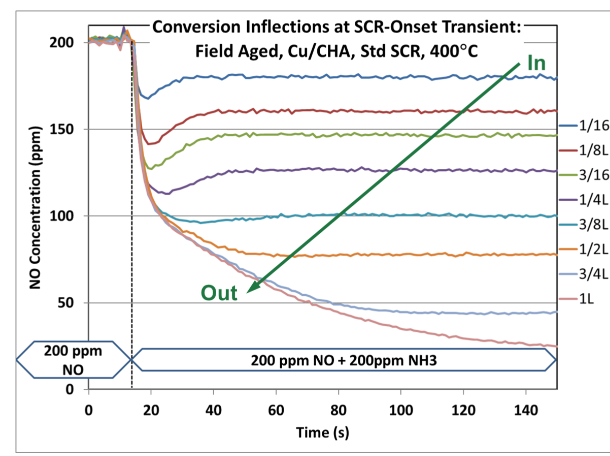




- Experimental 5-Step protocol probes SCR half-cycle components
- SpaciMS allows for spatial mapping of CI transients
  - Evolution of CI transient
  - Variations with concentrations & space velocity







Cu-Redox Model Shows CI Varies with Kinetic Parameters

Standard SCR

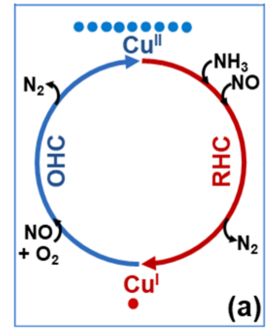
RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$

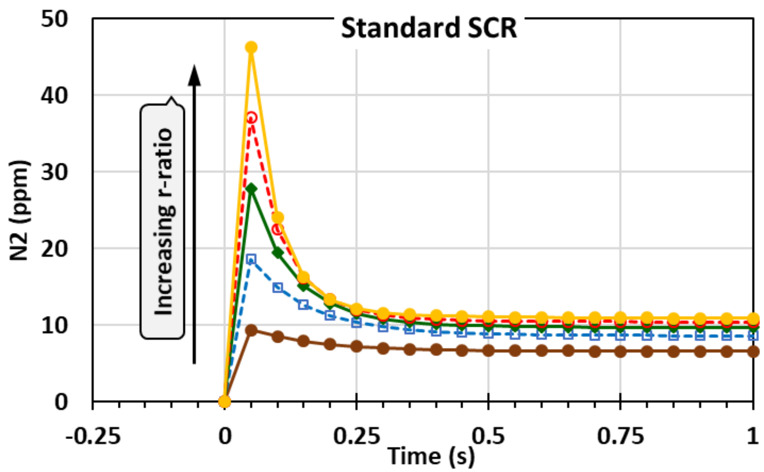
OHC: $2{\cdot}Cu^{I}(NH_3)_2 + O_2 + 2{\cdot}NO \rightarrow 2{\cdot}\ Cu^{II}(OH)(NH_3) + 2{\cdot}N_2 + 2{\cdot}H_2O$

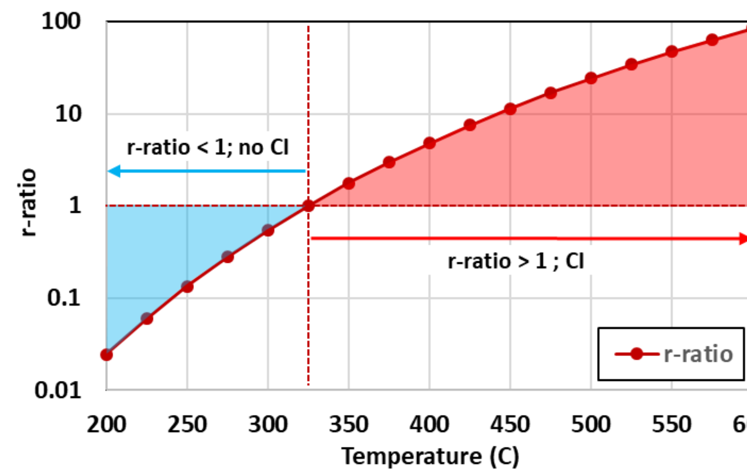
$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$

Net Standard SCR: $4{\cdot}NO + 4{\cdot}NH_3 + O_2 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$



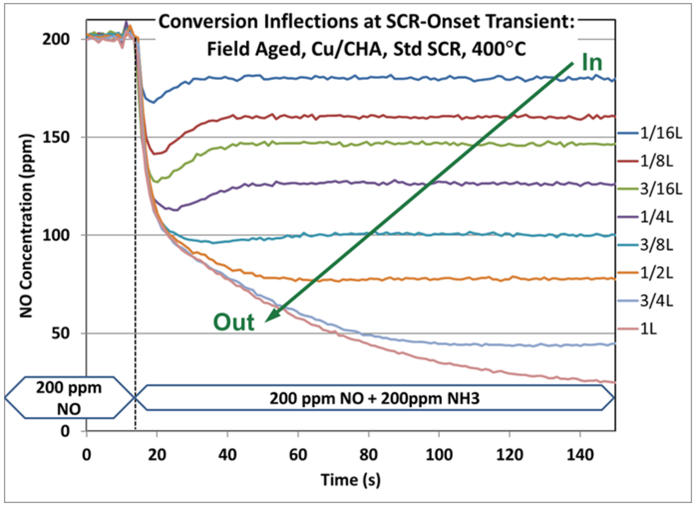
- Half-cycle models formulated for Standard & Fast SCR
  - Correct formulation & kinetic parameter set will accurately predict CI transient
- Predicted CI more distinct with increasing r-ratio & Temperature (r-ratio = r_{RHC} / r_{OHC})
  - Influence of specific E_a & A factors for RHC & OHC ($k = A\ e^{-Ea/RT}$)

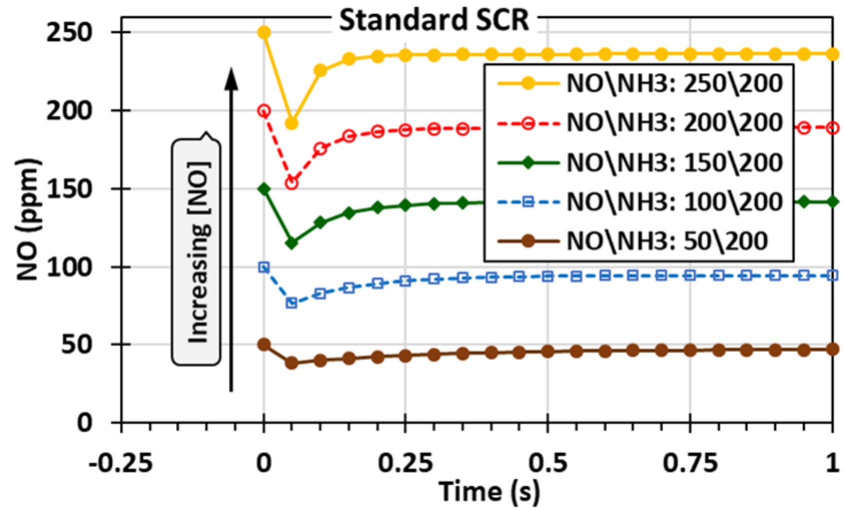




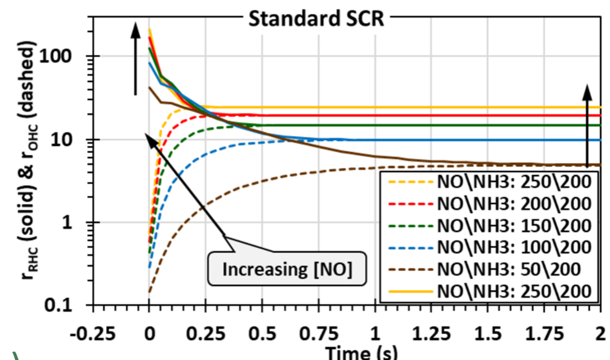
Oak Ridge National Laboratory | National Transportation Research Center | Cummins | JM Johnson Matthey Inspiring science, enhancing life

Cu-Redox Model Predicts Experimentally Observed Trends





- ***NO CI trends consistent with measured trends along catalyst axis***
  - Greatest CI at catalyst front (where NO is high)
  - CI degrades along catalyst as NO-conversion progresses

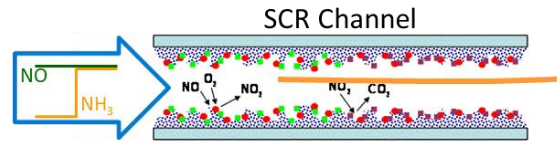


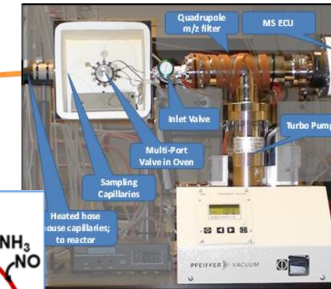
- Many other trends predicted by model
  - More distinct CI at higher temperatures
  - RHC & OHC rates converge at SS (mainly due to RHC slowing)

- ***Cu-Redox model accurately describes transient CI nature***
- ***Spatiotemporal measurements may be used to tune a kinetic model***

Technical Approach

1. Use Transient-Response Method to determine SCR kinetic parameters

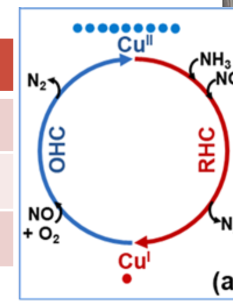




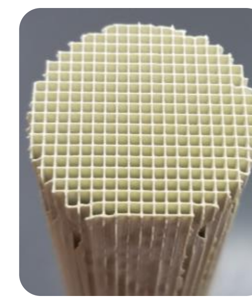
2. Measure CI transient shapes
   – 5-Step Protocol & spatiotemporal mapping

3. Fit RHC & OHC kinetic parameters
   – Using data & Cu-redox model

	RHC	OHC
E_a		
A		
k		



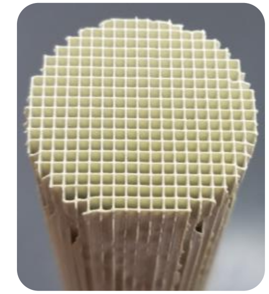
4. Baseline DeGreened catalyst kinetic parameters
   – Steps 2 & 3



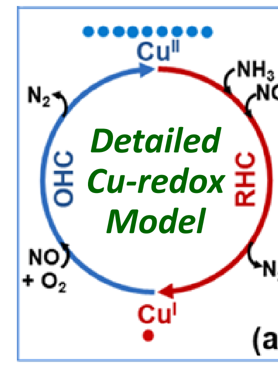
5. Study how ***Field Ageing*** impacts kinetic parameters
   – RHC & OHC specific impacts vs. DeG values
   – Pathways to improved durability and control

6. Study how Catalyst ***Formulation*** impacts kinetic parameters
   – Mechanistic origin of formulation benefits
   – Pathways to improved low-temperature aged performance

FY2019 Activities and Plans



- Measure CI for new state-of-the-art Commercial Cu-SSZ-13 SCR
  - DeGreened & Standard SCR conditions
  - 5-Step Protocol; Spatial & temperature sweeps
- Validate Cummins' In-House detailed model at higher local space velocities
  - AVL Boost; includes transport, kinetics, heat transfer
- Develop detailed half-cycle Cu-oxidation-state model (using AVL Boost)
  - Beyond conceptual and simple kinetic model of previous project
  - Use to fit Cu-redox half-cycle kinetic parameters



- Fit half-cycle kinetic parameters
  - DeGreened Cu-SSZ-13 in Standard SCR
  - RHC & OHC parameters

	RHC	OHC
E_a		
A		
k		

- Proof and refinement Pulsed-Response Experimental-Modeling method
  - Use in FY20 & 21 to quantify kinetic-parameter changes
  - Fundamental insights into field-ageing & formulation

Any proposed future work is subject to change based on funding levels

Remaining Challenges & Future Work

Key Challenge:

- Efficient catalyst performance under Field-Aged & Low-Temperature conditions
  - Mechanistic insights of how Ageing & Formulation impact SCR performance
  - Improved catalyst durability under Real-World Driving Conditions

Future Work:

- **FY20**: Kinetic study of Formulation & Field Ageing impacts
  - How ***Field Ageing*** impacts RHC & OHC vs DeG baseline Cu-SSZ-13
    - SCR-specific improvement concepts (e.g., dosing, formulation)
    - System-level improvement concepts (e.g., upstream oxidation catalyst)
  - Kinetic origins of ***Low-Temperature-Formulation*** benefits
    - Understanding performance benefits in the context of kinetic changes
    - Pathways for next-level formulation tuning

	RHC	OHC
E_a		
A		
k		

- **FY21**: Knowledge integration for improved low-temp aged SCR performance
  - Kinetic analysis of next-level low-temperature formulations
  - Assess pathways to improved catalyst durability
    - Using Cu-redox integrated into In-House model
  - Methods for catalyst-state assessment and control

Heavy Duty Emissions Regulations		
Current	2022	ca. '26/'27
Warranty (miles)	***Warranty*** (miles)	***Warranty*** (miles)
100,000 (5yr, 3k hr)	***350,000*** (5yr)	***800,000***

Solution Pathway

Any proposed future work is subject to change based on funding levels

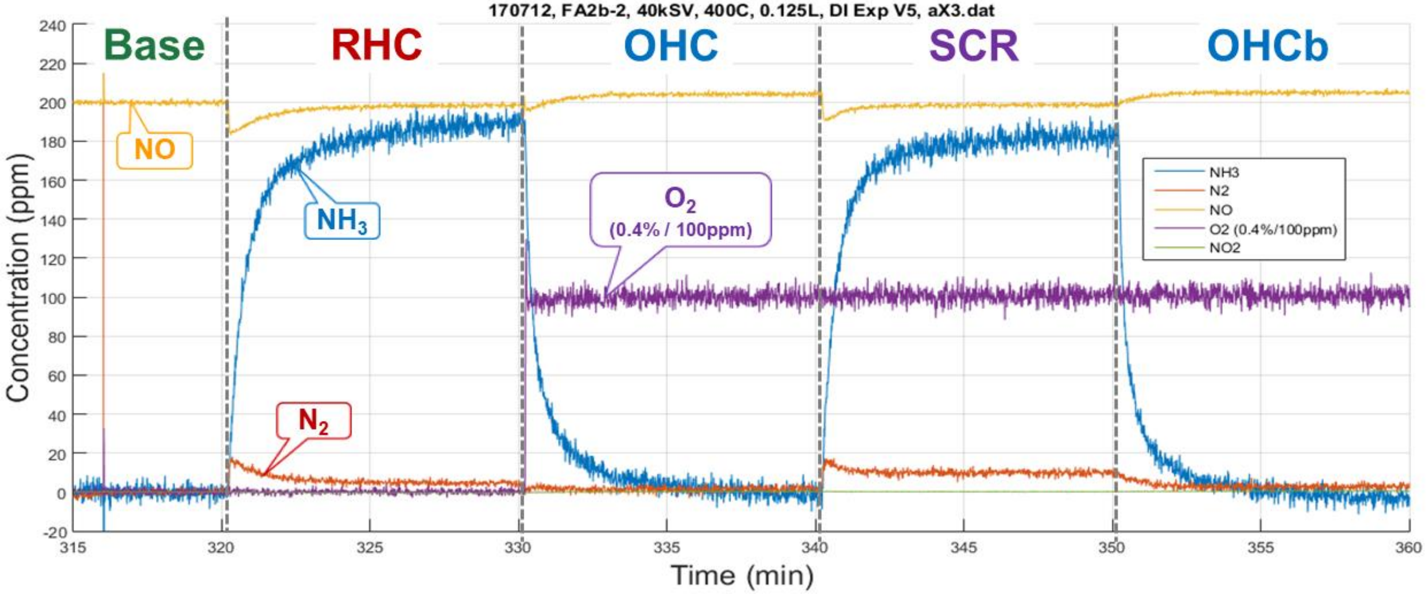
Oak Ridge National Laboratory | National Transportation Research Center | Cummins | JM Johnson Matthey Inspiring science, enhancing life

Summary

- **Relevance**
  - Focus is on kinetic origin of low-temperature performance and field aged SCR catalysts
  - Project work enables improved catalyst knowledge, models, design, OBD & control
  - Advances DOE goals for improved fuel economy, durability, & real-world emissions
- **Approach**
  - Apply experimental protocol to probe transient response of Cu-redox half-cycle steps
  - Develop and apply model to fit Cu-redox half-cycle kinetic parameters
  - Study kinetic impacts of low-temperature formulations and field-aged catalysts
- **Technical Accomplishments**
  - New project and CRADA established
  - Catalyst supplier, Johnson Matthey, incorporated into project as participant
  - FY19 plan to demonstrate pulsed-response method of determining kinetic parameters
- **Collaborations**
  - Johnson Matthey incorporated as project and CRADA participant
  - Communicate with community via presentations & publications
- **Future Work** (Any proposed future work is subject to change based on funding levels)
  - Determine kinetic origins of performance for low-temperature formulations
  - Determine impact of field-ageing on kinetics of commercial Cu-SSZ-13 SCR catalyst

Technical Back-Up Slides

5-Step Experimental Protocol for Studying Onset Transients

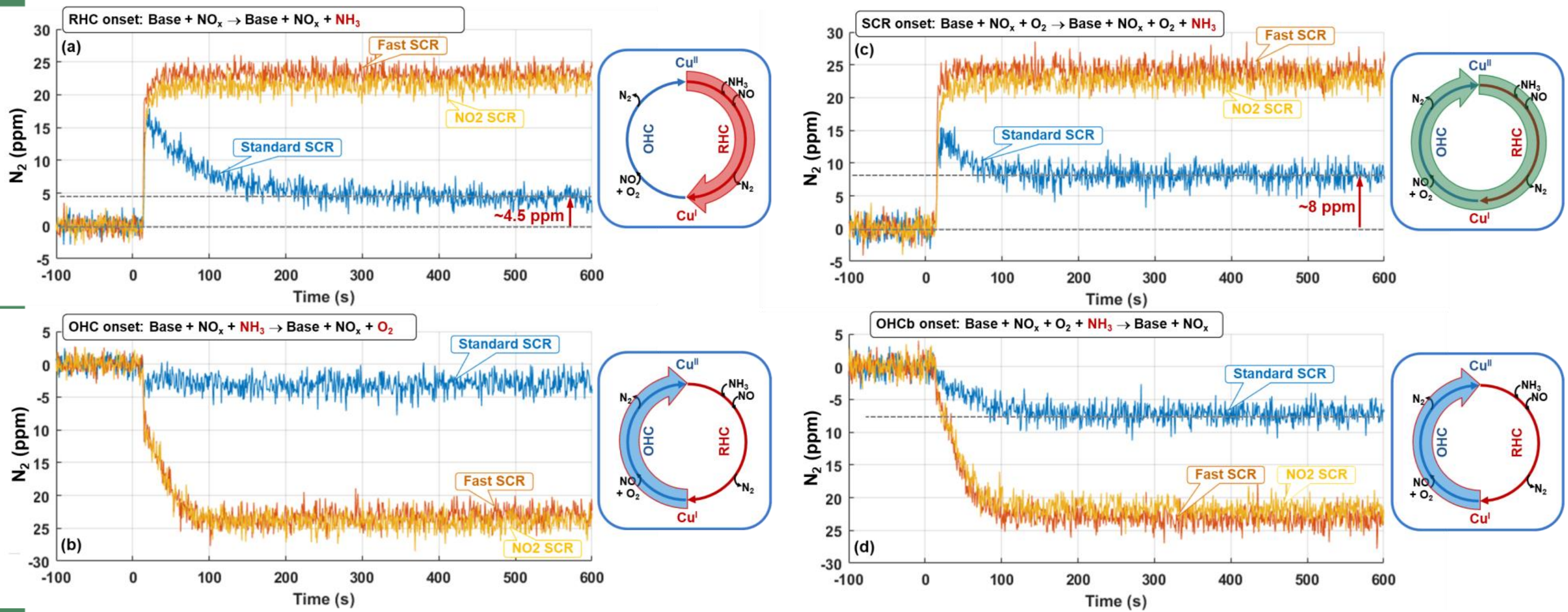


- Individual RHC, OHC & SCR transitions investigated
  - Step 1 - Base: 5% H_2O + 200ppm NO_x in Ar
  - Step 2 - RHC: Base + 200ppm NH_3
  - Step 3 - OHC: Base + 0.4% O_2
  - Step 4 - SCR: Base + O_2 + 200ppm NH_3
  - Step 5 - OHCb: Base + O_2
- Different SCR mixtures investigated
  - Standard, Fast & NO_2
  - 200ppm NO_x

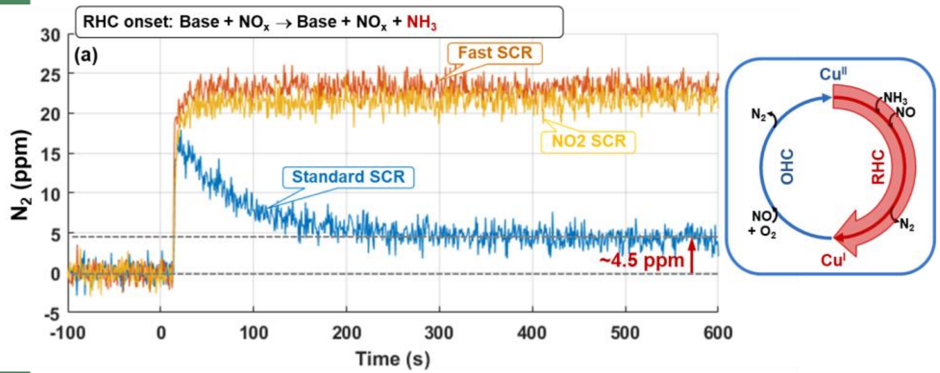
- Commercial SCR
- Field Aged: FA-2b
- 400°C
- 1/8L
- 40k SV

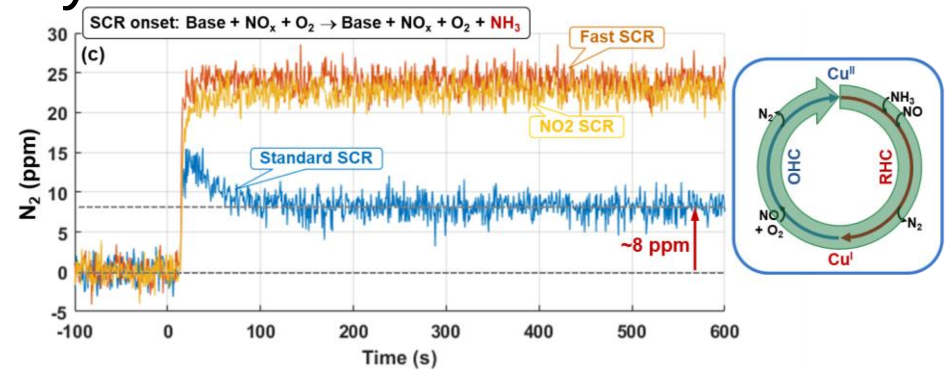
Oak Ridge National Laboratory | National Transportation Research Center
Cummins
JM Johnson Matthey
Inspiring science, enhancing life

Measured Half-Cycle Onset Transients



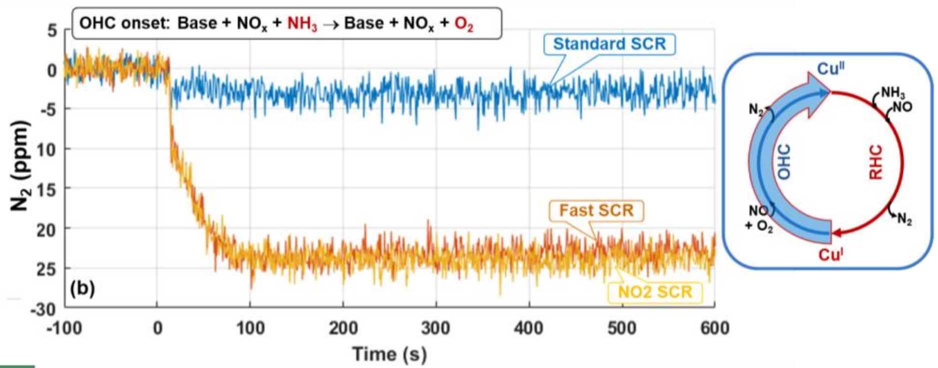
Measurements of Individual Half-Cycle Onset Transients

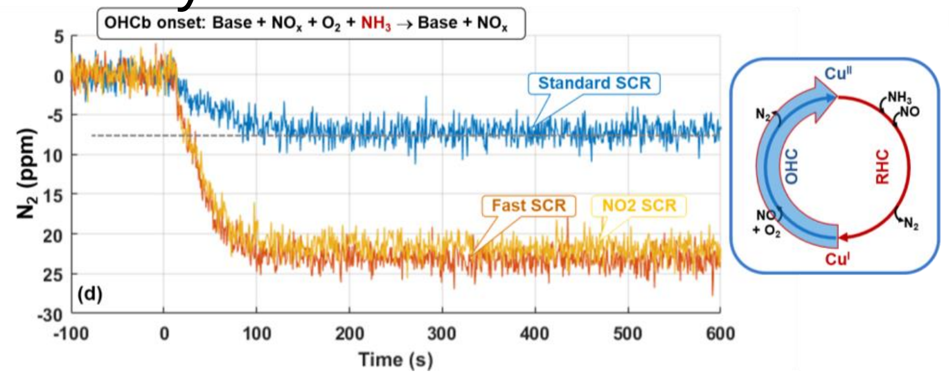




- 5-Step Experimental Protocol designed to study half-cycle onset transients & CI
  - Allows individual and combined half cycles to be probed (see Tech. Backup Slides)
- Standard SCR Onset Transients
  - RHC onset shows CI
    - Initial fast step-like transients indicates native RHC rate
    - Conversion degrades over ~200s as Cu^{II} is depleted
    - Non-zero SS due to contaminant or bulk oxygen driving OHC
  - For SCR onset
    - CI is smaller & faster, and SS conversion is greater
    - both half-cycles are active
- NO_2 & Fast SCR Onset Transients
  - Identical, fast, step-like transients without CI
    - Suggests OHC occurring via NO_2, and O_2 not participating
- OHC transients offer additional insights (see Tech. Backup Slides)

Measurements of Individual OHC Half-Cycle Onset Transients





- OHC Onset Transients
  - Starts from maximum [Cu^{I}] following RHC step
    - [Cu^{I}] greater than at OHCb start
    - Causes greater step-like onset vs. OHCb transient
  - NO_2 & Fast SCR transient are identical
    - Initially step-like, then slow over ~100s as Cu^{I} is depleted
  - Standard SCR show NO CI (see 5-Step Protocol figure)
    - Signal-to-noise is too small to resolve similar N2 CI
- OHCb Onset Transients
  - These follow SCR, and thus start from lower [Cu^{I}] initial condition
  - Slower Standard SCR transient (~150s) vs. NO_2 & Fast SCR (~100s)
    - Different OHC mechanism & kinetics for O_2- vs NO_2-driven OHC
  - NO_2 & Fast SCR transients are identical as with OHC
    - Suggests OHC driven by NO_2, and O_2 is practically inert

Half-Cycle based Model for Standard & Fast SCR

Standard SCR

RHC: $Cu^{II}(OH)(NH_3) + 2 \cdot NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$ (1)

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$ (2)

OHC: $2 \cdot Cu^{I}(NH_3)_2 + O_2 + 2 \cdot NO \rightarrow 2 \cdot Cu^{II}(OH)(NH_3) + 2 \cdot N_2 + 2 \cdot H_2O$ (3)

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$ (4)

Net Standard SCR: $4 \cdot NO + 4 \cdot NH_3 + O_2 \rightarrow 4 \cdot N_2 + 6 \cdot H_2O$ (5)

Fast SCR

RHC: $Cu^{II}(OH)(NH_3) + 2 \cdot NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$ (1)

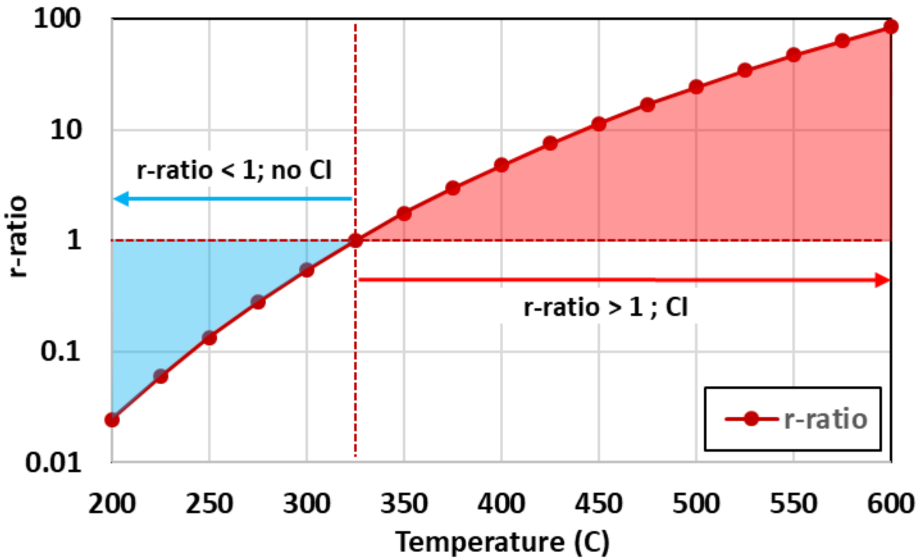
$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$ (2)

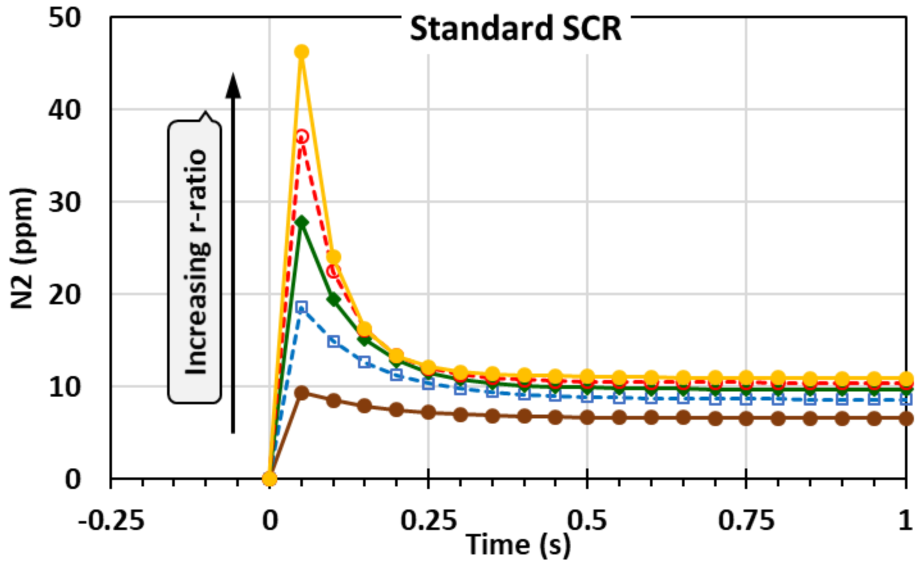
OHC: $Cu^{I}(NH_3)_2 + NO_2 \rightarrow Cu^{II}(OH)(NH_3) + N_2 + H_2O$ (6)

$r_{OHC} = k_{OHC} \cdot [Cu^{I}] \cdot [NO_2]$ (7)

Net Fast SCR: $2 \cdot NO + 2 \cdot NO_2 + 4 \cdot NH_3 \rightarrow 4 \cdot N_2 + 6 \cdot H_2O$ (8)

Global Model Predicts Consistent CI Nature & Trends

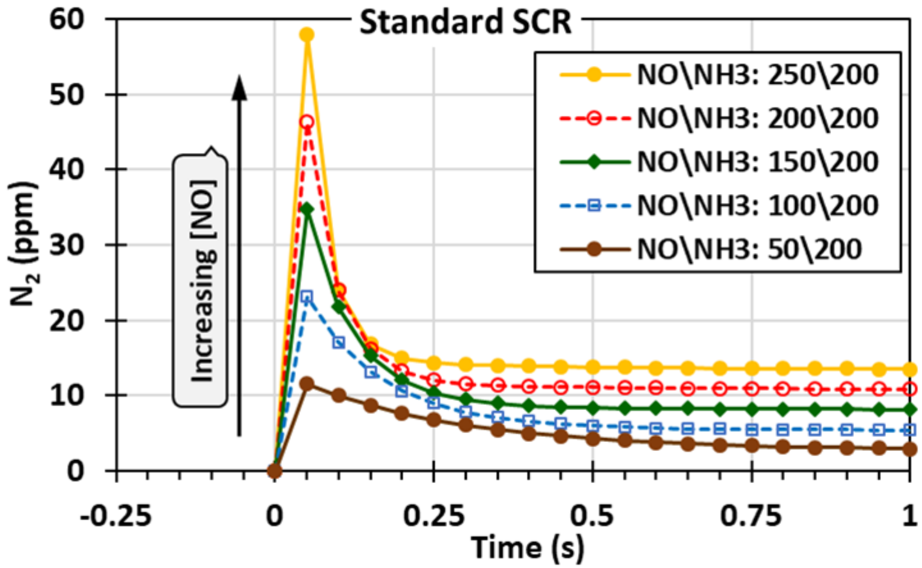


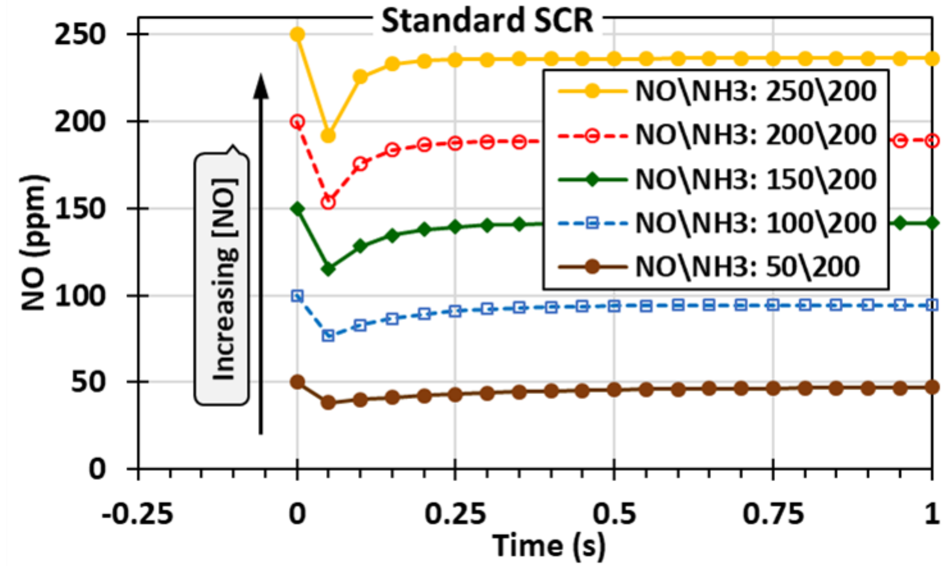


- Half-cycle model exercised to study how kinetic parameters influence CI
  - Model details shown in Tech. Backup Slides
- Ratio of half-cycle rates (r-ratio = r_{RHC} / r_{OHC}) increases with temperature
  - CI should be observed when r-ratio > unity
  - Unity crossing point tuned with RHC & OHC pre-exponential factors
- CI becomes more distinct with increasing r-ratio
  - Taller peak, faster tail
  - SS conversion increases with r-ratio
  - ***Temperature trend is consistent with experimental observations***
- ***CI nature varies with half-cycle kinetic parameters***

OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER
Cummins
JM Johnson Matthey Inspiring science, enhancing life

Global Model – CI varies with NO Concentration





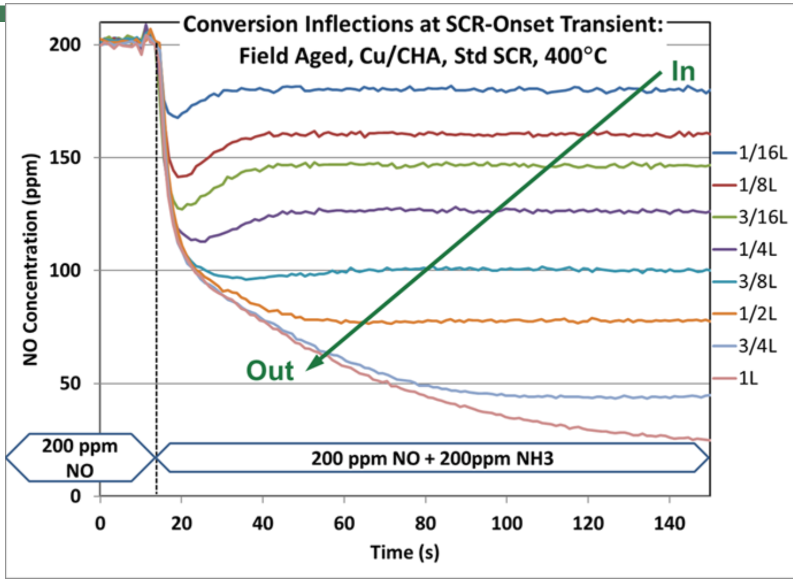
- Varying [NO] at constant 200ppm NH_3
  - CI independent of [NH_3], (zeroth order in [NH_3], see Tech. Backup Slides)
- CI becomes increasingly distinct with increasing [NO]
  - Similar for both N_2 & NO CI

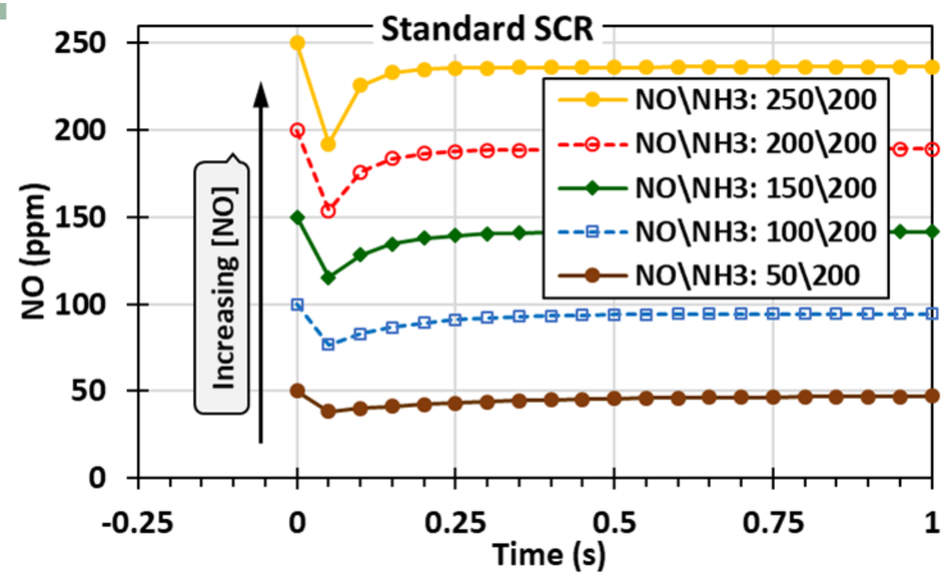
OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Cummins

JM Johnson Matthey Inspiring science, enhancing life

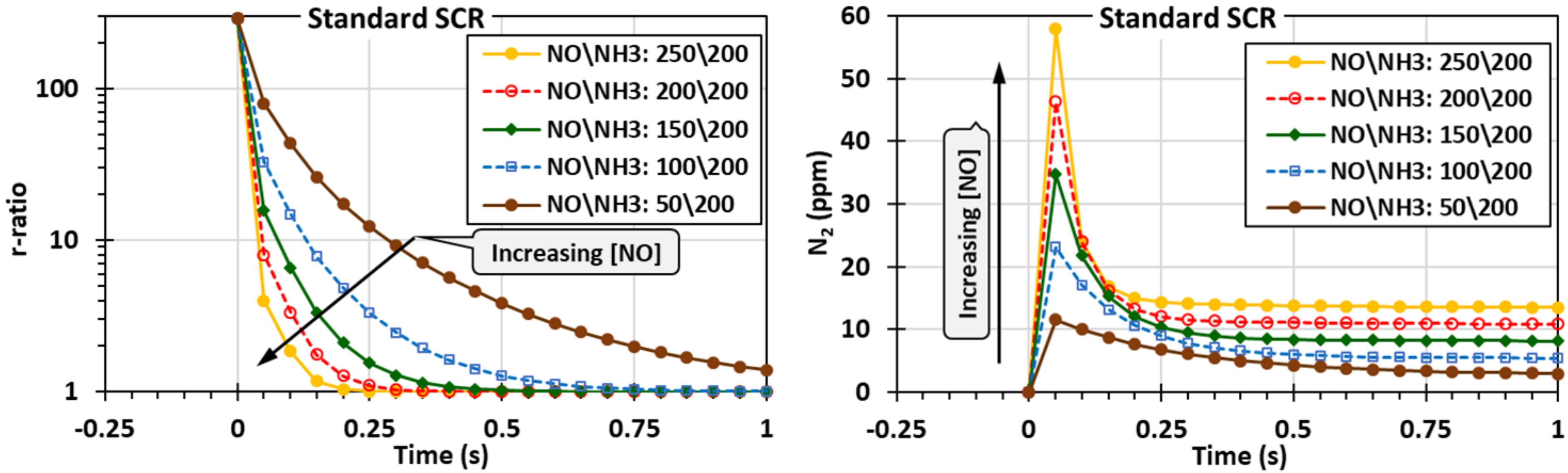
Global Model – CI varies with NO Concentration





- Varying [NO] at constant 200ppm NH_3
  - CI independent of [NH_3], (zeroth order in [NH_3], see Tech. Backup Slides)
- CI becomes increasingly distinct with increasing [NO]
  - Similar for both N_2 & NO CI
- ***NO CI trends consistent with measured trends along catalyst axis***
  - Greatest CI at catalyst front
  - CI degrades along catalyst as NO-conversion progresses
- ***Spatiotemporal measurements may be used to tune a global model***
  - Determine half-cycle kinetic parameters from fitting model to measurement data

Global Model – Half-Cycle Rates vary with NO Concentration



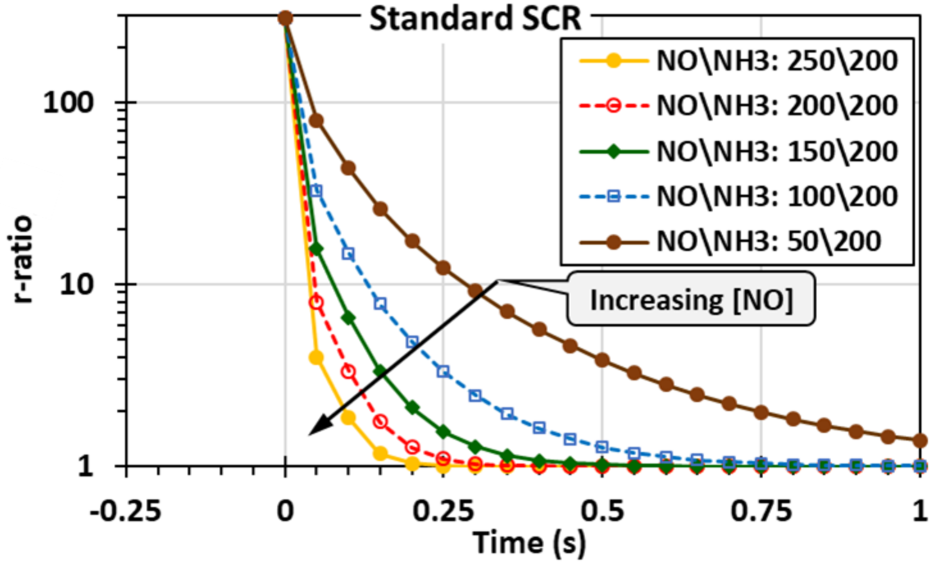
- r-ratio transient becomes faster with increasing [NO]
  - Distinct CI needs ***both*** r-ratio>1 ***and*** fast r-ratio transient

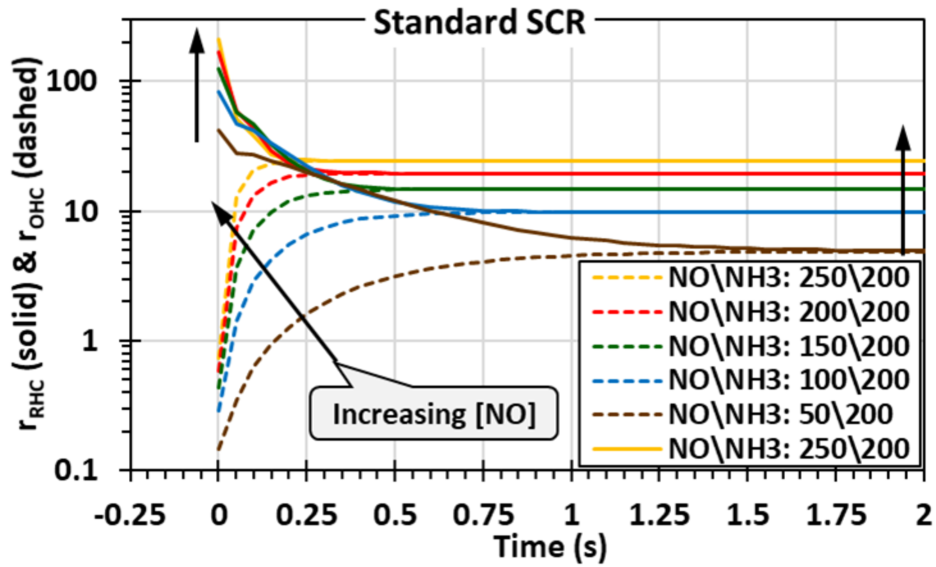
OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER

Cummins

JM Johnson Matthey Inspiring science, enhancing life

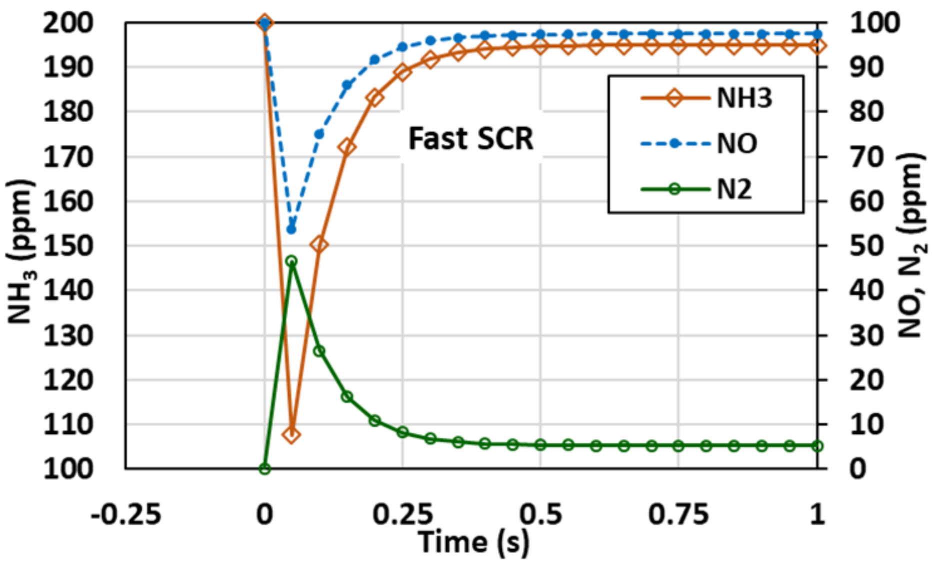
Global Model – Half-Cycle Rates vary with NO Concentration

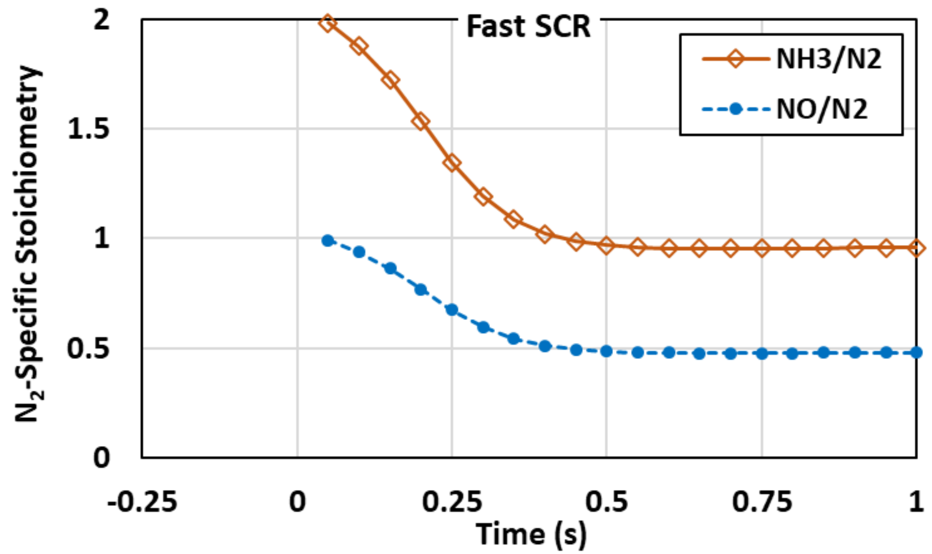




- r-ratio transient becomes faster with increasing [NO]
  - Distinct CI needs ***both*** r-ratio>1 ***and*** fast r-ratio transient
- RHC & OHC rates converge at steady state
  - Mainly due to RHC slowing
    - Relatively small r_{OHC} increase associated with increasing Cu^{I}
  - Greater SS conversion & rates with increasing [NO] ***(consistent with SpaciMS)***
  - Rate transient is greater when initial difference is greater
  - ***Half-cycle rate behavior is consistent with conceptual model***
- ***Model-based studies help advance CI understanding and nature***

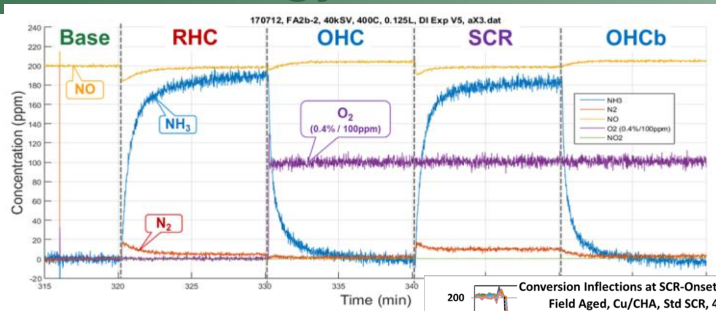
Global Model – Stoichiometry Varies Through CI Transient





- Model predicts CI for NO, NH_3 and N_2
- CI leading edge reflects RHC stoichiometry
  – RHC: $Cu^{II}(OH)(NH_3) + 2\cdot NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$
- Steady state reflects Net Fast SCR stoichiometry
  – Net Fast SCR: $2\cdot NO + 2\cdot NO_2 + 4\cdot NH_3 \rightarrow 4\cdot N_2 + 6\cdot H_2O$
- Stoichiometry transient reflects half-cycle balancing
  – As rates converge impact of the individual half cycles balance
- Generally similar results for Standard SCR (see Tech. Backup Slides)
- ***Technique can be use to validate model formulation***

Methodology for Formulating & Validating SCR Redox Model



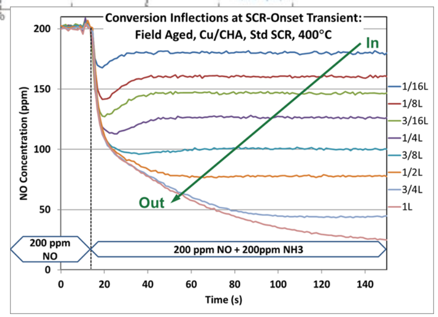
RHC: $Cu^{II}(OH)(NH_3) + 2 \cdot NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$

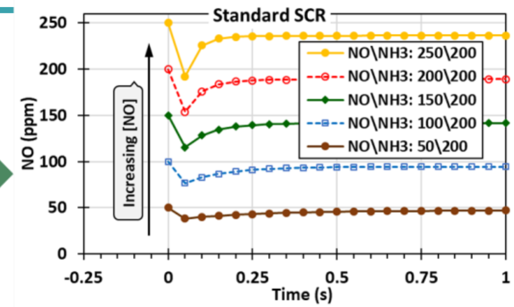
$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$

OHC: $2 \cdot Cu^{I}(NH_3)_2 + O_2 + 2 \cdot NO \rightarrow 2 \cdot Cu^{II}(OH)(NH_3) + 2 \cdot N_2 + 2 \cdot H_2O$

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$

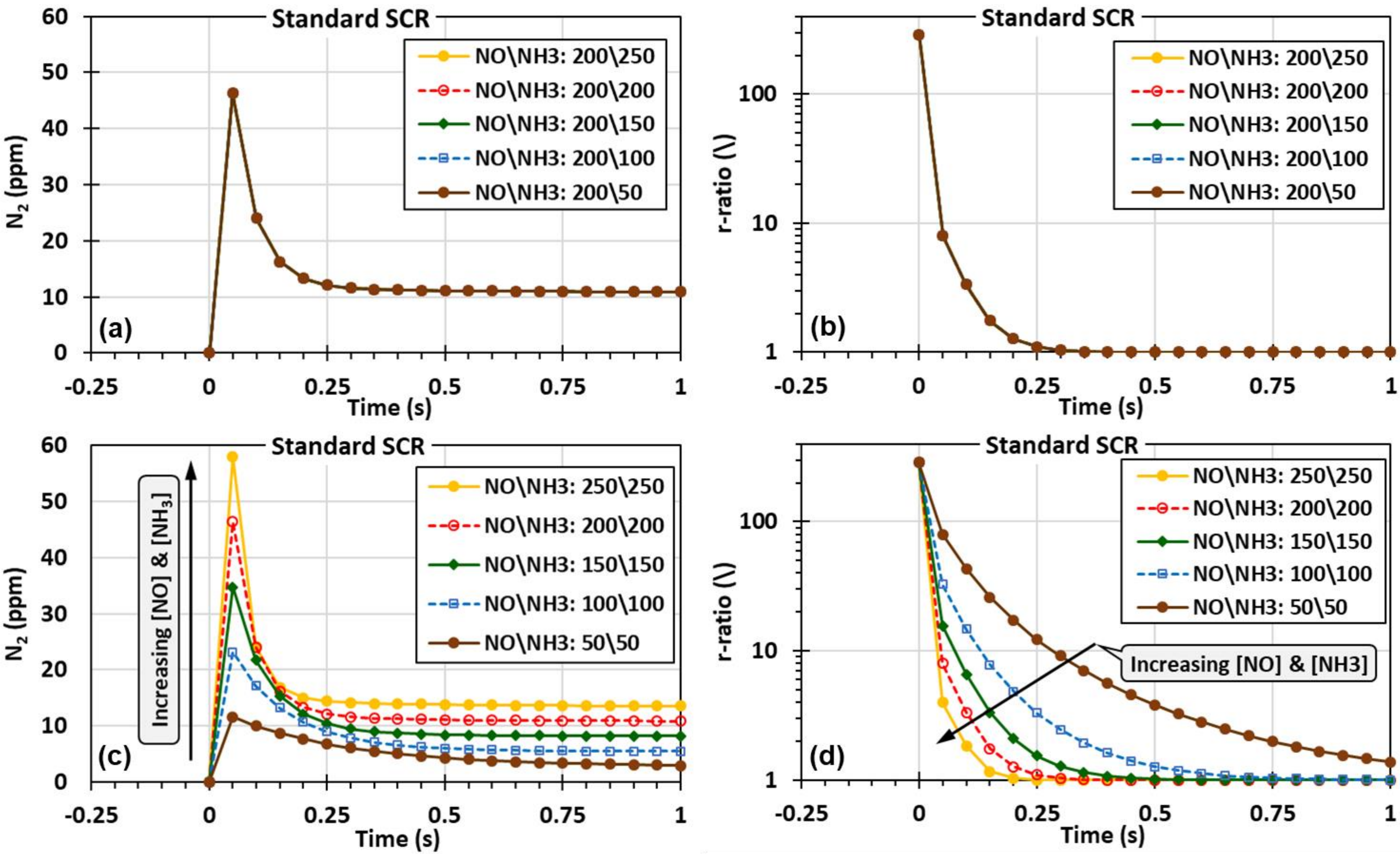
Net Standard SCR: $4 \cdot NO + 4 \cdot NH_3 + O_2 \rightarrow 4 \cdot N_2 + 6 \cdot H_2O$





- Step-response experiments to characterize CI & onset transients
  - Range of temperatures and concentrations
  - 5-Step Protocol to investigate individual & combined half cycles
  - ***Our measurements are the first to resolve half-cycle rate balancing***
- Formulate global SCR model based on the two half cycles
  - CI & transient nature varies with model formulation & kinetic parameters
    - Examples show broad dependence of transient performance on model parameters
    - Model CI trends are consistent with measurements
  - ***Our half-cycle model is the first to show this transient SCR nature***
- Use data to formulate, tune & validate the global SCR model – ***Next Steps***

Global Model – CI varies with [NO] but not with [NH_3]



Global Model – Stoichiometry Varies Through CI Transient